

Requested Patent: GB883256A
Title: HALOGENATION PROCESS ;
Abstracted Patent: GB883256 ;
Publication Date: 1961-11-29 ;
Inventor(s): ;
Applicant(s): COLUMBIA SOUTHERN CHEM CORP ;
Application Number: GB19590013797 19590423 ;
Priority Number(s): USX883256 19580502 ;
IPC Classification: ;
Equivalents: ;

ABSTRACT:

Halogenated hydrocarbons or derivatives thereof are prepared by providing a reaction zone at a halogenation temperature, establishing within the zone a moving gas stream flowing in a cyclic path, the countercurrently moving portions of the stream not being in contact, adding separately elemental halogen and the halogenatable material to the moving stream, and withdrawing a portion of the moving stream from the reaction zone at a point in the path of the stream remote from the points of addition of the reactants, while the remaining portion of the stream continues in a cyclic path, thereby comprising a principal component of the moving gas stream to which reactants are added and in which halogenation takes place. Normal halogenation conditions are used in the reaction zone. Reference is made to chlorination, bromination, fluorination and iodination, and mixed halogenations such as chlorination-fluorination. Suitable halogenatable materials include alkanes, unsaturated hydrocarbons, benzene, substituted benzenes such as phenol and xylenes, naphthalene and alkylated naphthalenes, and cycloaliphatic compounds, and their partially halogenated derivatives. Reference has been directed by the Comptroller to Specification 772,126.

PATENT SPECIFICATION

DRAWINGS ATTACHED

883,256



Date of Application and filing Complete Specification :
April 23, 1959.

No. 13797/59.

Application made in United States of America on
May 2, 1958.

Complete Specification Published November 29, 1961.

Index at Acceptance: Class 2(3), C1C(1A:1B:4:11A:12), C1D, C1E 5K(1:3:5:6), C1G1(A1:A2:B2:
C2A:C2B:C2X:D:E), C1G2A(1:2:4:5), C1G3(A:B), C1G4(A:B), C1G6A1.

International Classification: C07b.

Halogenation process.

COMPLETE SPECIFICATION

SPECIFICATION NO. 883,256

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Pittsburgh Plate Glass Company, a Corporation organised and existing under the laws of the State of Pennsylvania, United States of America, of One Gateway Center, Pittsburgh, Pennsylvania, United States of America.

THE PATENT OFFICE

DSD 067377/1(12) /R.109 200 9/62 TXL

ERRATA

SPECIFICATION NO. 883, 256

Page 3, line 27, for "principle" read "principal"

Page 6, line 64, for "anaylses" read "analyses"

THE PATENT OFFICE,
16th February, 1962.

DS 61219/1(7) /R.3537 200 2/62 PL

40 source or such material) as diluent is not
without operational inconveniences and
economic disadvantages. Providing such
diluent, for example, involves its separation
from the entire product composition, as by
45 rectification (fractional distillation). Rectifi-

40 tons to produce halogenated hydrocarbons 85
involve similar considerations.

It now has been discovered that the composition
of diluent for the gas phase halo-
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thereof, notably for gas phase chlorination 90

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C2A:C2B:C2X:D:E), C1G2A(1:2:4:5), C1G3(A:B), C1G4(A:B), C1G6A1.
International Classification: C07b.

Halogenation process.

COMPLETE SPECIFICATION

We, COLUMBIA-SOUTHERN CHEMICAL CORPORATION, a Corporation organised under the laws of the State of Delaware, United States of America, of One Gateway Center,

5 Pittsburgh, Pennsylvania, United States of America, (Assignee of Douglas Henry Eisenlohr), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be 50
10 performed, to be particularly described in and by the following statement:—

This invention relates to the production of halogenated hydrocarbons or derivatives thereof. More particularly it relates to the 55
15 production of halogenated hydrocarbons or derivatives thereof by gas phase reaction of the halogen and halogenatable materials.

It is known to produce chlorinated methanes (carbon tetrachloride, chloroform, 60
20 methylene chloride and methyl chloride) by gas phase reaction of methane or lower chlorinated methane and elemental chlorine. Although chemically the reaction appears straightforward, effective performance is not 65
25 necessarily of comparable simplicity. For example, gaseous mixtures of methane and chlorine having high chlorine concentration, e.g. in excess of 20 per cent by weight chlorine, may be hazardous, being prone to 70
30 be explosive or burn violently. This may necessitate conducting the chlorination in a gaseous mixture of low chlorine content or otherwise safeguarding against such hazards. Dilution of the gaseous reaction mixture 75
35 may be used. However, the selection and use of an appropriate diluent to provide suitable control of the reaction has its limitations. For example, the use of a portion of the reaction product composition (or other 80
40 source of such materials) as diluent is not without operational inconveniences and economic disadvantages. Providing such diluent, for example, involves its separation from the entire product composition, as by 85
45 rectification (fractional distillation). Rectifi-

cation includes condensation and vaporization steps. Diluent obtained by this separation in the liquid state eventually must be vaporized. On the other hand, should diluent be separated in a gaseous state, large 50
55 volumes of gases necessarily must be recycled. Either situation has economical limitations. Further complicating use of diluents is the influence of the diluent (chemical compositions) on the reaction. Depending upon the particular products which are desired, it may be advisable to control the chemical composition of the field if operation at optimum efficiency such as with minimized by-product formation, avoidance of excessive methane loss due to burning and the like is desired.

Another significant consideration for a highly effective methane chlorination process is that it be flexible and thus capable of 65
60 producing in varying ratios the various chlorinated methanes. Notwithstanding that all chlorinated methanes are commercial products, demands for each vary. A suitable process should preferably be sufficiently 70
75 flexible to permit production of chlorinated methanes in accord with demand. Should the character of the diluent influence materially effective chlorination and the products of chlorination, operational flexibility pursuant to demand variations may necessitate a corresponding change in the character of the diluent. To provide for appropriate diluent in such circumstances, it may be necessary to modify the product recovery 80
85 system, a change not always easily accomplished.

Similarly, halogenations of other hydrocarbons or partially halogenated hydrocarbons to produce halogenated hydrocarbons 85
involve similar considerations.

It now has been discovered that the composition of diluent for the gas phase halogenation of hydrocarbons or derivatives thereof, notably for gas phase chlorination 90

of methane and its partially chlorinated derivatives to produce chlorinated methanes, preferably should have a chemical composition approximately corresponding to the 5 reaction composition provided as a consequence of the halogenation, including by-products such as hydrogen chloride. This diluent should preferably comprise a major constituent, i.e., above 50 per cent by volume 10 and ideally at least about 70 per cent by volume, of the gaseous reaction mixture. Further desirable is performance of the reaction in a gas mixture containing a substantial halogen, preferably chlorine, concentration without the risk of establishing hazardous conditions.

According to the present invention there is provided a process for the production of 20 halogenated hydrocarbons or derivatives thereof which comprises providing a reaction zone maintained at a halogenation temperature, establishing within the zone a moving gas stream flowing in a cyclic path, the countercurrently moving portions of the 25 stream not being in contact, adding separately elemental halogen and the halogenatable material to the moving stream and withdrawing a portion of the moving stream from the reaction zone at a point in the 30 path of the stream remote from the points of addition of the reactants while the remaining portion of the stream continues in a cyclic path thereby comprising a principal component of the moving gas stream to 35 which reactants are added and in which halogenation takes place.

For the sake of convenience, the present invention is primarily described with reference to the halogenation, particularly the 40 chlorination, of hydrocarbons or partially halogenated hydrocarbons. The present invention is, however, in no manner so restricted and is applicable to any of the known gas halogenations.

45 In the process of the present invention, temperatures and other operational conditions may be varied, depending upon the materials to be halogenated and the desired halogenation products. The halogenation 50 is usually operated by so adjusting the amount of the diluent or portion of the stream which continues in the cyclic path that it comprises at least 5, preferably between 5 and 50, and for optimum results 55 between 5 and 30, times the volume of the halogen feed which is fed thereto. This degree of dilution is the consequence of increasing the rate at which the stream traverses its cyclic path relative to the 60 volume of halogen which is fed per unit of time. It is also preferred to operate the process with a pressure differential in the gas stream between two points in its cyclic path which causes or implements the cyclic movement of the gas stream.

The process of the present invention may be carried out in several types of reactors. For convenience the process will be described in more detail with respect to one such reactor which is shown in the accompanying drawing. 70

The apparatus includes a cylindrical tube 1 having most of its outer surface surrounded by a heating or cooling jacket 2 containing a circulating high temperature liquid heat transfer medium such as Dowtherm ("Dowtherm" is a Registered Trade Mark for a diphenyl-diphenylene oxide mixture). Temperature control of the liquid heat transfer medium in jacket 2 is provided by refluxing its vapours in water cooled condenser 3. Located within reactor 1 and disposed concentrically therein with respect to the longitudinal axis of reactor 1 is a tube 4. Tube 4 thus divides the reaction zone and reactor 1 into two principle sections, the first section A being within tube 4 and the second, section B, provided by the annulus between tube 4 and the outer walls of reactor 1 as well as the area not 80 enclosed by tube 4. At the inlet end of reactor 1 (at the left in the drawing) tube 4 tapers inwardly toward the inlet end of the reactor and terminates in a series of throats 5. Tube 6 of substantially smaller diameter 90 than tube 4 and concentric with the longitudinal axis of reactor 1 passes through nipple 8 and end wall 7 of the reactor into reactor 1, finally terminating in a jet 9. By 95 this means, the halogen, in this case chlorine is fed through feed tube 6 and jetted into tube 4 at a point 12 in tube 4 surrounded by throats 5.

Hydrocarbon feed means comprises the annulus defined by the volume between feed tube 6 and nipple 8 which opens into reactor 1. This provides for feeding hydrocarbon (or other halogenatable material) into the reactor separately from the halogen. The hydrocarbon thus enters through nipple 8 into the gas mixture in zone B of the reactor outside of tube 4. 105

End walls 7 and 10 terminate reactor 1. Halogen feed means 6 and hydrocarbon feed means 8 pass through end wall 7. Product withdrawal means 11 pass through end wall 10. 115

By virtue of the particular reactor design illustrated in the drawing, halogenation is most efficient and proceeds with surprising ease. Thus, elemental chlorine, as gaseous chlorine, may be jetted into tube 4 via feed means tube 6 and jet 9. By this jetting action, gaseous mixture in section B of the reactor circulates (i.e. is drawn) into tube 120 4 through throats 5 and is mixed there with chlorine. The hydrocarbon feed, introduced through nipple 8 into section B near throats 5 mixes with the gases in section B. Direct mixing of the hydrocarbon and feed 125 130

chlorine is thus prevented, avoiding risk of chlorine-hydrocarbon mixtures which may be hazardous.

Established by this reactor and feeding technique in tube 4 is a forwardly flowing stream in section A of the reaction zone. This stream, as it is initially constituted, includes halogen in this case chlorine, hydrocarbon and a recycle of gaseous mixture 5 discharged from tube 4 into zone B (as hereinafter explained further). As this gaseous reaction mixture discharges from the tube 4, gaseous mixture continues to be drawn through throats 5 into section A in 10 tube 4, and a major portion of the gas stream discharging from section A into section B of the reaction zone is returned to tube 4. The net result is a flow of gases (as indicated by the arrows) in section B 15 countercurrent to the flow of gases in section A and tube 4. The gaseous mixture in reactor 1 and sections A and B thus move in a cyclic repetitive path with countercurrent portions of the path being separated by 20 the walls of tube 4 to prevent substantial flow of gaseous mixture contrary to the principle cyclic path of flow. Product is withdrawn through removal tube 11, usually with the volume of product removal 25 corresponding to the volume of halogen, in this case chlorine and hydrocarbon being fed.

In the preferred operation of this reactor for halogenation, conditions are provided which develop a slight pressure differential 30 between the gases in section A and section B, preferably with the pressure in section A exceeding that of section B. The effect generated by jetting halogen into section A and throats 5, especially when the halogen 35 is fed at 0.5 to 100 pounds per square inch gauge pressure, develops such pressure differential. The pressures in sections A and B in reactor 1 may vary considerably, including subatmospheric and superatmospheric pressures. Illustrative pressures in the 40 reactor are between atmospheric and 100 pounds per square inch gauge. The maximum pressure differential between section A and section B (lowest pressure in section B and highest pressure in section A) usually 45 is no greater than 10 pounds per square inch, mainly ranging between 0.001 and 1 pound per square inch.

Also in halogenating with this reactor, 50 the volume of gases being drawn into tube 4 and section A from section B is usually 5 to 50 times the volume of the halogen jetted into tube 4 (section A) for most halogenations. Thus, the gases recycled and 55 used to dilute the halogen constitute by far the predominant portion of the gas reaction mixture.

Most halogenations involve greater 60 volumes of halogen than hydrocarbon feed. 65 Best rates of recycle are attained by jetting

the feed material which is greatest in volume, usually halogen. However, should the hydrocarbon feed be at a greater volume rate than the halogen feed, or should it be otherwise expedient, the hydrocarbon may 70 be fed through feed means 6 and the halogen fed through nipple 8. Thus, while in the preferred mode of operation gaseous elemental chlorine is jetted into tube 4 and the hydrocarbon is fed into and mixed with 75 the gas mixture in section B, the reverse may be practiced. Also, both feeds may be jetted.

For many of these halogenations an appreciable halogen concentration is maintained in the gas reaction mixture, both in sections A and B of the reaction zone. For example, in the halogenation of methane or partially halogenated methanes, the halogen concentration may be as high as 15 or 18 80 per cent by weight of the gas mixture in section A. In that portion of section A immediately after the halogen is mixed with the gas mixture drawn in from section B, the halogen concentration is maximum. As 85 the gas stream proceeds in its path of movement in section A, this halogen concentration drops as halogenation occurs. Since halogenation preferably occurs throughout the reactor, the halogen concentration continues 90 to drop in section B due to continuing reaction taking place. Thus, throughout its movement in a cyclic path, the gas stream experiences a gradual decline in halogen concentration from a maximum at the 95 point of halogen introduction to a minimum at the point in the cyclic path immediately prior to the addition of feed halogen. Where hydrocarbon is introduced into stream at a 100 point which is spaced considerably from the point of halogen feed (spaced with reference to the cyclic path of the stream) some dilution occurs in the halogen concentration. In most reactions, the effect of 105 this dilution does not significantly change the halogen concentration, or as in the performance of the reaction in the illustrated reactor, the point of hydrocarbon feed is essentially immediately prior to the point of halogen feed. Thus, there is a continuing drop in halogen concentration along the 110 cyclic path defined by the movement of the gas stream in the reactor.

The maximum halogen concentration may be as high as 50 per cent by weight. The 115 minimum halogen concentration is preferably 5 per cent halogen by weight of the gaseous mixture and, for optimum results, is at least 8 per cent halogen by weight. This is especially true in the halogenation of lower aliphatic hydrocarbons such as methane, ethane, propanes and butanes or their partially halogenated derivatives.

The process of the present invention is admirably suited for controlling the halo- 120 125 130

gen concentration in the moving cyclic gas stream in accordance with the preferences of any particular halogenation reaction. For the halogenation of methane, it has usually 5 been found advantageous to maintain the maximum halogen concentration on the order of 12 to 15 per cent halogen by weight of the gaseous mixture; this concentration being established at the point the 10 halogen feed is commingled with the gas mixture enriched with hydrocarbon feed as it enters the reaction section A. The gas mixture is discharged from section A into section B and as it leaves tube 4 usually 15 at halogen concentration several per cent less, e.g. 10 to 12 per cent halogen by weight, while the halogen concentration in section B prior to the mixing therewith of hydro- 20 carbon feed and introduction through throats 5 into tube 4 is still several per cent lower, e.g. in the range of 6 to 8 per cent halogen by weight.

In those halogenations such as methane halogenation preferably conducted in the 25 presence of a substantial halogen concentration in the reaction gases, the product gas composition withdrawn at 11 contains a substantial halogen concentration correspondingly approximately to the halogen concentration of the gaseous mixture being 30 discharged from tube A into zone B or corresponding in effect to the average halogen concentration in section B of the reactor. According to a further embodiment 35 of this invention, the halogen in the gaseous product mixture withdrawn from the reactor is consumed in a further halogenation. It usually is fed to a further zone at halogenation temperature. In this further re- 40 action zone or zones, the reaction is carried to completion in the sense that substantially all of the residual halogen present is consumed in conducting further halogenation.

Besides its simplicity, the process of the 45 present invention when conducted in a reactor of the type illustrated in the accompanying drawing has many distinctive features. It does not require premixing the halogen and hydrocarbon or derivatives 50 thereof feed prior to entry into the reaction zone, thus avoiding any possibility of hazardous halogen, particularly chlorine, and methane mixture. It is further distinctive in utilizing as diluent or principal component 55 of the gas reaction medium, a gaseous mixture having a composition corresponding to the product composition the process is specifically operated to provide. Since often the entire gaseous product mixture is an 60 exemplary diluent, the diluent (or reaction medium) is generated in situ and directly available as generated for use as diluent, thereby circumventing complicating problems of rectifying the gaseous reaction product composition and recycling portions. 65

The flexibility of the procedural steps in being self-adjusting (flexible) to operational conditions best suited for producing varying products is most evident.

Further features include requiring only 70 the introduction to the reactor of halogen and the material to be halogenated. Diluent or other materials need not be fed to the reactor. Any need for diluting the respective feed materials, notably the halogen and 75 halogenated materials, prior to their introduction into the reactor is circumvented. They may instead be directly and separately fed to the reactor.

The process of the present invention is 80 generally applicable to a wide variety of gas phase halogenation processes and hence to the halogenation of halogenatable materials broadly. Thus, while the process is particularly effective and most efficient 85 with regard to substitution halogenations its principles are beneficial when applied to performance of additive halogenations as well as effective both to additive and substitution halogenation. Besides chlorinations, 90 halogenations, notably bromination, fluorination and iodination, or even mixed halogenation such as chlorination-fluorination, 95 may be accomplished by means of the process of the present invention.

The process of the present invention is suited to gas phase halogenation of halogenatable organic materials exemplified by aliphatic compounds containing from 1 to 6 carbon atoms and having at least 1 hydrogen atom available for substitution halogenation. Examples of compounds which can be halogenated are:—methane, ethane, propane, isopropane, the butanes, the pentanes, longer chain hydrocarbons and mixtures thereof as well as their partially chlorinated derivatives such as methyl chloride, methylene chloride, chloroform, monochloroethane, 1,2-dichloroethane, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, 1,1,1,2-tetrachloroethane and pentachloroethane as well as corresponding partially chlorinated derivatives of other hydrocarbons and mixtures of one or more of any such chlorinatable materials. Also halogenatable are the unsaturated hydrocarbons such as acetylene, ethylene, 1,2-butylene and the like. Thus, the process of the present invention is of value in the chlorination of materials which in the gas phase may be chlorinated both by addition and substitution. Besides the aforementioned chlorinatable materials, other chlorinatable organic compounds, particularly those chlorinatable by substitution chlorination, may comprise a significant, preferably principal, portion or even all of the chlorinatable feed. Corresponding partially brominated, even fluorinated or otherwise halogenated (including mixed halo- 130

generated, e.g., chlorofluoro materials) are included.

Gas phase halogenations, especially chlorinations, of still other organic compounds 5 may be performed using the process of the present invention. Benzene, substituted benzenes such as phenols, xylenes, and other aromatics such as naphthalene and alkylated naphthalenes, may be halogenated. 10 Either nuclear or ring halogenation and/or halogenation of halogenatable ring substituents are possible, e.g., aralkyls such as ethylbenzene may have the ethyl and/or ring chlorinated. Also included are cycloaliphatics 15 such as cyclopentane, cyclohexane, cyclopentene, and cyclopentadiene. Similarly, the partially halogenated derivatives of aromatic, aralkyl and cycloaliphatics may be more fully halogenated. 20 As the diversity of halogenations which may be performed indicates, the process may be operated with extreme flexibility. For example and with reference to the specific reactor, the jacket may serve either 25 to cool or to heat the reaction mixture. It is thus possible to perform reactions under essentially isothermal conditions.

Temperatures developed in the reactor are those which are well recognized for the 30 proper halogenation of the material to obtain the desired product or products. Thus, in the chlorination of methane to produce a reaction mixture predominating in carbon tetrachloride, the optimum temperatures 35 are between 500°F. and 900°F. When the principal product desired from methane is methyl chloride, the optimum temperatures are 700°F. to 800°F. In the case of ethane chlorination to produce product 40 positions principally comprised of 1,1-dichloroethane, the temperatures are of the order of 500°F. to 700°F. Furthermore, when the chlorinatable material is a partially chlorinated product such as methyl chloride, 45 some variation in the preferred temperature is also possible. For example, in the chlorination of 1,1-dichloroethane to produce a reaction mixture predominantly of trichloroethane, the principal component of which 50 is 1,1,1-dichloroethane, temperatures between 500°F. and 700°F. are used with success.

The ratio in which the material to be 55 halogenated and halogen, either gaseous or liquid, are fed to the reactor is in part determined by the product or products sought. If carbon tetrachloride is to be the principal product from methane, the ratio should be approximately 2 to 4 moles of 60 chlorine per mole of methane. Correspondingly, the mole ratio to chlorinatable materials is adjusted when the product contains less chlorine than carbon tetrachloride. For example, when chloroform is desired 65 from methane, the mole ratio of chlorine

to methane is lower, generally averaging less than 2 to 1. A certain portion of the methane may be unchlorinated.

Recovery and separation of product or 70 products from the gaseous composition produced (besides further reaction of the residual halogen) may involve selective condensation of the organic constituents of the gaseous composition following which the liquid mixture of the halogenated products 75 may be rectified by recourse to appropriate distillation techniques. It may further be advisable to treat the halogenated organics with small amounts of alkali such as sodium carbonate, sodium hydroxide or the like to 80 neutralize small quantities of acid, notably hydrohalic acid, which remain. Many chlorinated organic compounds, particularly the chlorinated aliphatic hydrocarbons of 1 to 6 carbon atoms, are capable of dissolving very small but, nevertheless, finite amounts of water. If removal of all or a significant portion of this water is advisable, it may be accomplished by drying the chlorinated organics by the use of drying agents such as 85 calcium chloride.

The process of the present invention may 90 be illustrated in, but is in no manner limited to the following Examples.

Example I

The reactor used was of the type illustrated in the accompanying drawing. It included a cylindrical nickel tube 5 feet long and 4 inches in internal diameter sealed at one end except for an outlet nickel pipe 2 inches in diameter and concentric with the longitudinal axis of the main reactor tube. This reactor tube was jacketed with a tube 4 feet long and 6 inches in diameter. The inlet end of the reactor tube was sealed with a 4 inch nickel flange. Welded to this nickel flange was a 1 inch diameter nickel pipe-tee, concentric with the major longitudinal axis of the reactor. The tee was assembled so that the hydrocarbon could be fed to the reactor in the annulus around the pipe opening up into the reactor and the annulus around the inlet to the jacket.

The chlorine feed means comprised a $\frac{3}{8}$ inch diameter pipe concentrically disposed around a longitudinal axis of the reactor, passing through the nickel tee and flange, terminating in a jet outlet surrounded by throats. The jet assembly contained a jet and three throats which jet assembly terminated in a tube 4 feet long and 2 and $\frac{1}{2}$ inches diameter disposed in the axial centre of the reactor. In these experiments, the gaseous chlorine was preheated by passage in heat exchange relationship with the Dowtherm in the reactor jacket. This means the chlorine gas was at about the temperature of the Dowtherm. Chlorinatable feed material was introduced at 70°F. to the reactor. Chlorine was fed at 0.5 to 15 130

pounds per square inch gauge pressure and the chlorinatable material was fed at atmospheric pressure. The methane was fed at 70°F.

5 The gaseous product mixture discharged from this reactor was led into a further reaction zone maintained at appropriate chlorination temperature. The reaction zone was provided by a Dowtherm A jacketed 10 reactor 2 inches in diameter and 6 feet long. Reaction of the residual chlorine was effected there.

From this second reactor the gaseous reaction mixture was fed to a shower pipe 15 provided by a column of pipe having four sections. At the bottom, it had a 4 inch diameter sump with an inlet pipe from the second reactor and a product overflow line with liquid seal. Immediately above this 20 section was a 4 inch diameter, 24 inch high packed section and a tube and shell water-cooled condenser set on top of the packed section. The top section was a 4 inch diameter pipe containing a cold thimble filled 25 with dry ice-acetone. Thus, the gases emanating from the second reactor were partially condensed by the downwardly flowing stream of liquids condensed in the upper section, serving primarily to condense the organic 30 components, notably the chlorinated hydrocarbon, while some traces of the lights of mostly methyl chloride or methane and hydrogen chloride pass overhead of gases. The water cooled condenser section removes 35 most of the sensible heat with reflux and condenses about 2/3 of the product while the cold thimble reduces the dew point

so that vent hydrogen chloride contains only small traces of methyl chloride and methylene chloride. The overhead gases, mostly 40 hydrogen chloride, were led to a hydrogen chloride absorber, a water cooled packed 2 inch glass pipe and then to a caustic scrubber comprised of a 2 inch glass pipe packed with $\frac{1}{2}$ inch Berl saddles. Bottoms from the 45 shower pipe were collected as product.

In operation, this reactor was employed by first heating with Dowtherm (diphenylene-diphenylene oxide mixture) overnight 50 while setting the temperature of the Dowtherm by control of the nitrogen pad pressure. Nitrogen was fed to purge the system and thereafter feed of hydrocarbon was commenced, following which chlorine feed was started. As soon as the hydrocarbon feed and chlorine were regulated properly, dry ice and acetone were placed in the cold 55 thimble of the shower pipe. Product (bottoms) from the shower pipe was in each of the runs weighed and sampled. After thoroughly washing this sample with water and sodium carbonate, the sample was dried by filtration through the soda ash. Chromatographic analyses of the products were then obtained.

Following the above procedure, using 60 methane or methyl chloride as the hydrocarbon or partially halogenated hydrocarbon feed and chlorine as the chlorinating agent, the chlorination to provide higher chlorinated methane and methyl chloride was performed in a plurality of runs. The following 65 Table 1 lists the operational data and experimental data:

TABLE I					
75 Dowtherm Temperature, °F.	675	675	675	675	
Recycle Reactor Temperature, °F.	677	683	684	684	
Soaking Reactor Temperature, °F.	665-670	665-670	670-675	663-667	
Hydrocarbon or partially Halogenated Hydrocarbon Feed	CH ₃ Cl	CH ₃ Cl	CH ₃ Cl	CH ₄	
Operating Time of Run, hours	5.5	7.75	7.5	5.0	
Moles Cl ₂ Per Mole Hydrocarbon or partially Halogenated Hydrocarbon	2.13	2.13	1.675	—	
Hydrocarbon or partially Halogenated Hydrocarbon Feed, pounds per hour	0.636	0.71	0.934	—	
Chlorine Feed, pounds per hour	1.91	2.13	2.2	2.1	
Product, pounds per hour	1.127	1.635	1.683	0.862	
Retention Time (seconds)					
Recycle Reactor	3.55	3.18	3.08	3.55	
Soaking Reactor	19.2	17.2	15.3	Approx. 20	
Unreacted Chlorine Concentration (per cent by weight of the mixture)					
100 Recycle Reactor	11.2	14.3	12.6	14.1	
Soaking Reactor (second)	2.1	2.1	2.1	3.3	

(Table 1 continued)

Products (mole per cent of chlorinated products)					
5	Carbon Tetrachloride	74.3	51.2	50.9	96.3
	Methyl Chloride	0.1	0.2	0.3	Trace
	Methylene Chloride	4.7	10.8	1.7	1.4
	Chloroform	20.2	37.7	46.9	1.6
	1,1-Dichloroethane	0.6	Trace	Nil	Trace
	Heavies	Trace	Trace	Trace	0.6
10	Yields, Based On:				
	Hydrocarbon Feed or partially Halogenated Hydrocarbon	62.3	87.9	66.9	—
	Feed (per cent of feed)	78.8	99.0	99.1	75.3
	Chlorine Feed (per cent of feed)				

15 In the above runs of Example I, the jet of chlorine through the throats resulted in recycling above 20 volumes of the product reaction mixture plus hydrocarbon per volume of the chlorine introduced into the reactor.

20 This ratio of recycle volume to chlorine feed volume is based upon a calibration with air fed to the jet. Anemometer readings were obtained for the jet alone and for the jet in the reactor at pressures on the jet of 0.5 to 70 psig. The ratio is the volume of gas issued by the inner chamber A versus the volume of gas issued by the

25

jet. It will be understood that those operational details described in terms of volume recycle are based upon such reference measurement. 30

Example II

The reactor and procedure described in Example I were employed feeding 1,1-dichlorethane as the chlorinatable organic material primarily to provide trichloroethanes and predominantly 1,1,1-trichloroethane. The following Table II tabulates the operational data and results of several runs:

40

TABLE II

	Dowtherm Temperature, °F.	695	650	625	625
	Recycle Reactor Temperature, °F.	—	630	603	601
	Soaking Reactor Temperature, °F.	693	638	607	609
	Operating Time, hours	5.5	7.5	6.0	4.5
45	Moles of Cl ₂ Per Mole C ₂ H ₄ Cl ₂	0.456	0.697	0.697	0.561
	C ₂ H ₄ Cl ₂ , pounds per hour	3.27	4.0	3.0	4.0
	Cl ₂ , pounds per hour	1.0	2.0	1.5	1.61
	Product, pounds per hour	—	4.16	2.77	4.34
	<i>Retention Time (seconds)</i>				
50	Recycle Reactor	—	3.2	4.4	2.7
	Soaking Reactor	8.7	11.4	15.5	13.6

*Unreacted Chlorine Concentration,
(per cent by weight of reaction
mixture)*

55	Recycle Reactor Outlet	—	17.0	16.0	—
	Soaking Reactor Outlet	—	1.5	2.1	—
<i>Products (mole per cent of chlorinated products)</i>					
60	1,1-C ₃ H ₄ Cl ₂	53.7	31.4	32.7	37.6
	1,1,1-C ₃ H ₄ Cl ₃	18.2	38.3	38.5	38.2
	1,2-C ₃ H ₄ Cl ₂	1.7	2.2	2.9	1.4
	1,1,2-C ₃ H ₄ Cl ₃	8.2	11.9	14.3	9.9
	1,1,1,2-C ₃ H ₄ Cl ₄	1.2	6.0	6.4	5.8
	1,1,2,2-C ₃ H ₄ Cl ₄	Trace	Trace	Trace	Trace
65	Miscellaneous Impurities	17.0	10.2	5.2	7.1

WHAT WE CLAIM IS:—

1. A process for the production of halogenated hydrocarbons or derivatives thereof which comprises providing a reaction zone 5 maintained at a halogenation temperature, establishing within the zone a moving gas stream flowing in a cyclic path, the counter-currently moving portions of the stream not being in contact, adding separately elemental halogen and the halogenatable material to the moving stream and withdrawing a portion of the moving stream from the reaction zone at a point in the path of the stream remote from the points 10 of addition of the reactants while the remaining portion of the stream continues in a cyclic path thereby comprising a principal component of the moving gas stream to which reactants are added and in which 15 halogenation takes place.

2. A process as claimed in Claim 1 in which there is a pressure differential in the gas stream between two points in its cyclic path which causes or implements the cyclic 20 movement of the gas stream.

3. A process as claimed in Claim 1 or 25 in which the reaction zone comprises two sections, the elemental halogen being introduced into the first section, the halogenatable 30 material being added to the gases in the second section, the halogen and the gas mixture from the second section being mixed and diluted in the first section, the gas mixture from the first section being 35 discharged into the second section thus providing for the gaseous mixture in the second section supplied to the first section, and withdrawing from the second section and reaction zone a portion of the gas mixture.

4. A process as claimed in Claim 3 in which the second section of the reaction 40 zone surrounds the first zone.

5. A process as claimed in Claim 3 or 45 in which the pressure maintained in the first section of the reaction zone is greater than the pressure in the second section.

6. A process as claimed in any of Claims 1 to 5 in which the halogen is introduced 50 into the reaction zone at a pressure of from 0.5 to 100 pounds per square inch gauge.

7. A process as claimed in any of Claims 1 to 6 in which the pressure in the reaction zone is from atmospheric pressure to 100 pounds per square inch gauge.

8. A process as claimed in any of Claims 55 4 to 7 in which the pressure differential between the two sections of the reaction zone is no greater than 10 pounds per square inch.

9. A process as claimed in Claim 8 in which the pressure differential between the two sections of the reaction zone is between 0.001 and 1 pound per square inch.

10. A process as claimed in which there 60 are present at least 5 volumes of gas com-

position per volume of halogen at the introduction of the halogen.

11. A process as claimed in Claim 10 in which there are present between 5 and 50 volumes of gas composition per volume 70 of halogen at the introduction of the halogen.

12. A process as claimed in Claim 11 in which there are present between 5 and 30 volumes of gas composition per volume of halogen at the introduction of the halogen. 75

13. A process as claimed in any of Claims 1 to 12 in which the gas stream undergoes a gradual decline in the halogen concentration from a maximum at the point 80 of halogen introduction to a minimum at the point in the cyclic path immediately prior to introduction of feed halogen.

14. A process as claimed in any of Claims 1 to 13 in which the maximum 85 halogen concentration is 50 per cent by weight of the gaseous mixture.

15. A process as claimed in any of Claims 1 to 14 in which the minimum halogen concentration is 5 per cent by weight 90 of the gaseous mixture.

16. A process as claimed in Claim 15 in which the minimum halogen concentration is 8 per cent by weight of the gaseous mixture. 95

17. A process as claimed in any of Claims 1 to 16 in which the reaction product is led to a further reactor to produce further halogenation thereof.

18. A process as claimed in any of Claims 1 to 17 in which the halogen is chlorine. 100

19. A process as claimed in any of Claims 1 to 18 in which the halogenatable material is a hydrocarbon or partially halogenated hydrocarbon. 105

20. A process as claimed in any of Claims 1 to 19 in which the halogenatable material is an aliphatic compound containing from 1 to 6 carbon atoms and having 110 at least 1 hydrogen atom available for substitution halogenation.

21. A process as claimed in Claim 19 or 20 in which the aliphatic compound is methane or a chlorinated methane. 115

22. A process for the production of halogenated hydrocarbons or derivatives thereof substantially as hereinbefore described with particular reference to the foregoing Examples.

23. Halogenated hydrocarbons or derivatives thereof whenever produced by a process as herein described and claimed. 120

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949 to patent No. 772,126.

883,256 COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale.*

